



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(54) Title:</b> DESTRUCTURED FUMED SILICA FOR USE AS A HIGH CLARITY ADDITIVE  |           |   |
| <b>(57) Abstract</b><br><p>A fumed silica having an average aggregate size of less than .09 <math>\mu\text{m}</math>, a bulk density greater than 2.5 lbs/ft<sup>3</sup> and is characterized by its destructured nature. Also disclosed is a polyolefin composition of high clarity containing an effective amount of fumed silica made in accordance with the present invention.</p> <div data-bbox="1065 1565 1948 2670"><p>250nm 100K<br/>TS720 7F153<br/>BALL MILLED<br/>1 HOUR</p></div>   |           |   |

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TITLE**DESTRUCTURED FUMED SILICA FOR USE  
AS A HIGH CLARITY ADDITIVE**BACKGROUND OF THE INVENTION5      1.      Field of the Invention.

The present invention relates to fumed silica and, more particularly, to fumed silica for use as a nucleating and clarifying additive in thermoplastic compositions.

2.      Background of the Invention.

10      Polyolefin resins are widely used in the production of packaging for sundries, containers, industrial parts and the like by virtue of their excellent mechanical and chemical properties, as well as their hygienic safety. In addition, polyolefin resins are particularly suited for mass production because they can be molded easily. It is commonly known to add nucleating agents to certain polyolefins materials, such as polypropylene, to increase the rate of production, enhance physical properties, and  
15      improve the optical qualities of the polymer by modifying crystallization behavior.

Enhanced clarity or transparency and reduced haze and gloss are also aesthetic features of increasing importance during the manufacture of polyolefin compositions. Clarity, for example, is important in such items as household containers or housewares, household cleaners, personal care items, syringes, test tubes and other  
20      medical devices and the like.

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In general, clarity is not an inherent property of polyolefin plastics, most of which are more or less opaque due principally to their partially amorphous or crystalline nature. Most polyolefins, however, do have some degree of crystallinity and, as such, are typically referred to as semicrystalline. It is generally accepted that high clarity is related to a low degree of crystallinity. The number and size of the crystals also become important. Large crystals, in theory, reduce clarity as a result of light diffraction and scattering. As a result, polyolefins of good and enhanced clarity should possess crystal sizes at or smaller than the wavelength of visible light to prevent light scattering and thus, opacity. It is also generally acknowledged that the performance of a nucleating agent is, to a certain extent, dependent upon its degree of dispersion in a particular polymer melt. As a result, it is desirable that the nucleating agents be in as fine a form as possible. Mechanical delumping, and other conventional size reduction devices are typically used to achieve a 1 to 10 micron powder. For an overview of size reduction technology, please see Kukla, "Understand Your Size-Reduction Options," *Chemical Engineering Progress*, pp. 23-35 (May 1991) and Hixon, "Select An Effective Size-Reduction System," *Chemical Engineering Progress*, pp. 36-44 (May 1991).

Various additives for polyolefins, typically known as nucleators or nucleating agents, are known to promote crystallization. See, for example, U.S. Patent Nos. 5,135,975 and 5,049,605 to Rekers, et al., and U.S. Patent No. 4,314,039 to Kawai et al., and U.S. Patent No. 4,016,118 to Hamada. Also known as a sub-type of nucleating agents are clarifying agents which, in addition to improving processibility, substantially enhance the clarity of the polyolefin. See, for example, U.S. Patent No. 5,198,484 to Mannion, U.S. Patent No. 4,808,650 to Titus et al., U.S. Patent No. 4,483,952 to Uchiyama and U.S. Patent No. 4,371,645 to Mahaffey.

Conventionally, nucleators have therefore been added to accelerate the crystallization of thermoplastic compositions, as well as enhancing the impact resistance, rigidity, tensile strength and transparency of such compositions. Broadly speaking, nucleators have been grouped into inorganic types, e.g. calcium carbonate,

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zinc fluoride, cadmium fluoride, talc, alumina and silica, and organic types, such as stearates, adipic acid, sebacates, aliphatic acid salts, benzoic acid salts, phenylsulfonic acid and the like. Although these types are generally known to be nucleating agents, it is recognized that not all nucleating agents have the same degree of effectiveness and in fact, have no effect in some thermoplastic systems. For example, in U.S. Patent Nos. 4,321,357 and 4,321,357, fumed silicas and zinc oxide were found to have no effect in injection moldable amide-imide polymers and were useless as nucleating agents. At the present time, it has been found that sodium benzoate and substituted sorbitols are the most common types of nucleating agents.

Sodium benzoate is the salt of benzoic acid and is frequently used as a nucleating agent in polyolefin compositions such as polypropylene. It has been found successful in the injection molding of polypropylene to improve processing (by reducing fabrication time) and enhance some of the performance characteristics. However, sodium benzoate is not an efficient clarifying agent.

Similarly, substituted sorbitols provide improved processibility while increasing the aesthetic value by increasing clarity, i.e. reducing the amount of haze. However, the use of sorbitols, like sodium benzoate, in plastics has resulted in several deficiencies, such as the transfer of unacceptable taste and odor to a contained material, plate-out in the mold at high processing temperatures, narrow molding temperature window, yellowing and inconsistent performance with different grades of material due to the presence of residual catalysts.

Prior art nucleating agents have resulted in polyolefin compositions having improved clarity, resistance to shrinkage and heat resistance, and improved physical and mechanical properties. There is, however, a need for further improvements and alternatives, particularly with respect to aesthetic features such as odor and yellowing,

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and processibility, such as broadening the molding temperature range and reducing plate-out. It is therefore an object of the present invention to produce a cost-effective, clarifying and nucleating agent which overcomes the problems associated with existing nucleating and clarifying agents.

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### SUMMARY OF THE INVENTION

The present invention is directed to a fumed silica having an average aggregate size of less than 0.09 micron, and in a preferred embodiment, an average aggregate size ranging from 0.01 to 0.05 micron. The fumed silica is further characterized as having an increased bulk density and its destructured nature. The fumed silica is particularly adapted for use as an effective nucleating and clarifying agent in thermoplastic compositions.

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Another aspect of the invention are masterbatch compositions and dispersions for use in further polymer compounding which incorporate the fumed silica described above. Still another aspect are thermoplastic compositions incorporating such fumed silicas.

These and other aspects of the present invention will become more apparent from the detailed description described herein.

### BRIEF DESCRIPTION OF THE DRAWINGS

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FIGURE 1 is a transmission electron micrograph (100,000X magnification) showing the structure of a typically commercially available fumed silica treated with polydimethylsiloxane oil.



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FIGURE 2 is a transmission electron micrograph (100,000X magnification) showing the destructured fumed silica of the present invention treated with polydimethylsiloxane oil.

5       FIGURE 3 is a transmission electron micrograph (100,000X magnification) showing the structure of a commercially available fumed silica having a BET surface area of  $200 \pm m^2/g$ .

FIGURE 4 is a transmission electron micrograph (100,000X magnification) showing the fumed silica of Example 3 which has been destructured in accordance with the present invention.

10       FIGURE 5 is a histogram showing the aggregate size distribution of the fumed silica shown in Figure 3.

FIGURE 6 is a histogram showing the aggregate size distribution of the fumed silica shown in Figure 4.

15       FIGURE 7 is a plot of crystallite diameter on the x-axis versus the percentage of light transmitted on the y-axis.

FIGURE 8 is a plot of silica size on the x-axis versus crystallite size on the y-axis.

#### DETAILED DESCRIPTION OF THE INVENTION

20       The production of fumed silica is a well-documented process which involves the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen.

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Molten particles of roughly spherical shapes are formed in the combustion process, the diameters of which are varied through process parameters. These molten spheres of fumed silica, typically referred to as primary particles, fuse with one another by undergoing ballistic collisions at their contact points to form branched, three dimensional chain-like aggregates. The force necessary to break aggregates is considerable and often considered irreversible. During cooling and collecting, the aggregates undergo further collision that may result in some mechanical entanglement to form agglomerates. Agglomerates are thought to be loosely held together by Van der Waals forces and can be reversed, i.e. de-agglomerated, by proper dispersion in suitable media.

Although it is theorized that the diameters of the silica sphere particles typically range from about 0.07 to 0.3 micron, it is useful to point out that such particles can not be individually obtained from currently available technology and commercially available fumed silica has an average aggregate size ranging from 0.09 to 0.13 micron, as illustrated in Figures 1 and 3.

The fumed silica of the present invention has an average aggregate size of less than 0.09 micron and preferably, less than 0.07 micron and is characterized by its destructured nature and high bulk density. "Average" is defined to be the number mean equivalent spherical particle diameter and is sometimes referred to as DCircle. By "destructured" it is meant that the fumed silica aggregates are physically fractured or broken as illustrated in Figures 2 and 4. For comparison purposes, Figure 1 shows a high magnification TEM of the same fumed silica as that in Figure 2. Note that the fumed silica of Figure 1 possesses the branched chain-like aggregate structure of fused spherical primary particles. Although the small primary particles are still discernable in Figure 2, the fused branched chain aggregate structure of fumed silica is clearly segmented into much smaller aggregate sizes. Similar comparisons can be



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made between Figures 3 and 4. Preferably, the fumed silica is as destructured as possible in order to reduce the aggregate size and enhance its effectiveness as a nucleating agent in thermoplastic compositions.

5 The destructured fumed silica of the present invention can further be characterized by its aggregate size distribution as illustrated in Figures 5-6. Figure 5 is a log normal distribution of the commercially available fumed silica having an average or mean aggregate size of approximately 129.4 nm. Figure 6, on the other hand, shows the fumed silica of Figure 5, except that it has been destructured in accordance with the present invention. As is readily noted, the average aggregate  
10 size of the destructured fumed silica of Figure 6 is reduced to 90.5 nm. Although it is recognized that particle and aggregate size measurements are not an exact science, it can be easily seen that, upon comparison of the two distributions in Figures 5 and 6, that the aggregate distribution is shifted significantly to the lower aggregate size. As a result, the fractions of smaller sized aggregates is increased while the fractions  
15 of larger aggregates is reduced. In a preferred embodiment, not only is the average aggregate size less than 0.07 micron, but the maximum size of any individual fumed silica aggregate is small as possible, and preferably less than 0.4 micron.

The aggregate size distribution of the present invention was chiefly determined by transmission electron microscopy (TEM). In this method, a fumed silica sample  
20 is dispersed in a liquid medium until the fumed silica agglomerates have been reversed to aggregates. Its concentration is then adjusted until discrete aggregates are shown on the TEM grid. Multiple fields on the grid were then imaged using an image analysis system manufactured by Kontron and stored on a video tape until greater than 1000 aggregates were imaged and stored. The stored images were in  
25 turn fed into an image analysis computer with a frame-grabber board for further processing, i.e. cleaning up aberrations, adjusting background and normalizing the

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image. Individual particles in the binary field are finally measured for a number of primary particle sizes and aggregate size and shape parameters were calculated. Measurements may be recalled individually or in the form of statistical or histogram distributions.

5           The fumed silica of the present invention can be hydrophilic or hydrophobic, untreated or treated. Hydrophobic silica can be produced by treating a fumed silica, which by its nature is hydrophilic, with a suitable treating agent which will vary depending on the desired degree of hydrophobicity and other characteristics. It is also  
10       recognized by those skilled in the art that hydrophilic fumed silicas may also be treated with the appropriate agents. Whether rendering the fumed silica either hydrophilic or hydrophobic, the treating agent is any suitable structure that is compatible with the thermoplastic composition to be nucleated. Examples of typically treating agents include straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or amides, nitriles, ethers, silanes,  
15       siloxanes and polymers derived therefrom. By compatible is meant that the agent treated silica can be readily and uniformly dispersed into the thermoplastic composition and then act as an effective nucleation site upon cooling from the melt during production. Furthermore, when a dispersant is also desirable, the treated fumed silica should serve to compatibilize the dispersant with the thermoplastic  
20       composition.

          The fumed silica of the present invention can be destructured by subjecting it to extreme/severe mechanical forces/stresses such that fumed silica aggregates are fractured into sub-micron pieces. In one embodiment, mills such as tube mills, cone mills, cylinder mills and ball mills may be used to impart the necessary stress on the  
25       fumed silica. It is preferred that stress be of sufficient force to substantially decrease the aggregate size to less than 0.09 micron and preferably to less than 0.07 micron.

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As the destructuring process takes place, the bulk density of the fumed silica is significantly increased from its commercially available density of between 2.5 and 3.0 lbs/ft<sup>3</sup> to greater than 10 lbs/ft<sup>3</sup>, and preferable to greater than 20 lbs/ft<sup>3</sup>. It will be recognized by those skilled in the art that the time it takes to destructure the fumed silica in accordance with the present invention will vary depending on the type of mill, size of mill, and velocity of the mill. As a result, milling should continue until the desired average aggregate size and bulk density is achieved. Similarly, over-milling of the fumed silica should be avoided to prevent agglomeration of the fumed silica which tends to make the fumed silica difficult to disperse under normal shear conditions.

It has also been observed during the destructuring process that the surface area, as measured by the nitrogen adsorption method of S. Brunauer, P. H. Emmet, and I. Teller, J. Am. Chemical Society, Volume 60, Page 309 (1938) commonly referred to as BET, is reduced. It should be noted that the reduction in surface area is unexpected since the surface area is controlled by the size of the primary particles, which is not anticipated to change during the milling step. However, it is theorized that the normally rough surface of the primary particle may be smoothed out during the milling operation, thereby resulting in a decreased surface area.

In the alternative process, the fumed silica of the present invention can be produced directly in a dilute flame of hydrogen and oxygen during the hydrolysis of the silicon tetrachloride vapor. It has been found that the size of the fumed silica primary particles and aggregates are governed by the inter-relationship between the concentration of the precursor, temperature and time histories. By controlling the concentration of different diluents while maintaining a uniform temperature profile for the particles to grow, i.e. growth region, the size of the primary particles and aggregates can be controlled. Further growth of the particles can be prohibited by

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rapidly cooling the particles with a high velocity quench of air. It should be noted that the fumed silica, when produced in the flame, will typically have a bulk density lower than 2.5 lbs/ft<sup>3</sup> and will often range from about 0.8 lbs/ft<sup>3</sup> to about 2.5 lbs/ft<sup>3</sup>.

5 The fumed silica of the present invention is particularly useful as a nucleating and clarifying agent in thermoplastic systems, particularly polyolefin compositions. The polyolefin polymers of the present invention may include aliphatic polyolefins and copolymers made from at least one aliphatic olefin and one or more ethylenically unsaturated comonomers. Generally, the comonomers, if present, will be provided in a minor amount, e.g., about 10% less or even about 5% or less, based upon the weight of the polyolefin. For example, a typical polypropylene copolymer will contain about 3% ethylene. Such comonomers may serve to assist in clarity improvement of the polyolefin, or they may function to improve other properties of the polymer, such as fabrication characteristics, impact strength and/or other physical properties. Examples include ethylene, propylene, hexene, octene, acrylic acid, 10 methacrylic acid, and esters of the same, vinyl acetate, etc. Preferably, the polyolefin compositions contain from about 2 to about 6 carbon atoms and have an average molecular weight of from about 10,000 to about 2,000,000, preferably from about 30,000 to about 300,000. Examples of such polyolefin compositions include polyethylene, linear low density polyethylene, polypropylene, crystalline 20 ethylene/propylene copolymer (random or block), poly(1-butene) and polymethylpentene. The polyolefins of the present invention may be further described as semi-crystalline, basically linear, regular polymers which may optionally contain side chains, such as are found in conventional low density polyethylene. Other polymers which may benefit from the destructured fumed silica of the present invention include polyethylene terephthalate, glycol modified polyethylene 25 terephthalate, polybutylene terephthalate, polystyrene, polyamides, polyimides and liquid crystal polymers, typically referred to as LCD's.

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Clarifying properties are conferred when the destructured fumed silica of the present invention is formulated into the polyolefin composition in a quantity within the range of 0.1 to 1.0 % by weight. A preferred range of 0.15 to 0.35 % by weight has been found effective to decrease haze, thereby increasing clarity. It should be noted that the use of a destructed fumed silica is anticipated to reduce clarity in thermoplastic systems because of its refractive index and aggregate size distribution. Therefore, the use of the fumed silica in accordance with the present invention as an effective nucleating and clarifying agent is truly unexpected.

Other additives may also be used in the composition of the present invention, provided that they do not interfere with the primary benefits of the invention. It may even be advantageous to premix these additives with the nucleating agent in order to enhance dispersion and distribution during melt processing. Such additives are well known in the art and include for example, plasticizers, anti-static materials, lubricants such as waxes, calcium stearate, stearic acid, glycol monostearate, catalyst neutralizers, antioxidants, fillers, light stabilizers, colorants, other nucleating agents and the like. Some of these additives may further provide beneficial physical characteristics such as improved aesthetics, easier processing, and improved stability in processing or end use condition.

Although the present invention has been directed to fumed silica, it has been found that any material, when meeting certain criteria, can be particularly adapted for use as an effective nucleating and clarifying agent. Through extensive study and investigation, conceptual plots have been developed to help define and establish this criteria. Certain polymers, like polypropylene, are semi-crystalline in nature, thereby having a certain degree of crystallinity. The crystallites, in turn, are of a certain size, the size being controlled by the nucleating agent. Crystalline polypropylene is higher in density and has a refractive index that is slightly higher than amorphous



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polypropylene. The polypropylene crystallites will scatter the incident light, the amount of scattering being dependent on the size of the crystallites, the number of crystallites, and the delta in the refractive indices of the crystalline and amorphous phases. The end result is a molded polypropylene part having a reduction in the amount of light transmitted and thereby being more opaque. The amount of light transmitted through a known thickness is a measure of the clarity.

Applying the principles of the Rayleigh light scattering theory, Figure 7 illustrates the fraction of light transmitted versus the volume average crystallite size. The calculations were performed for polypropylene assuming an estimated delta of 0.0025 in the refractive indices, a typical wavelength for white light of 550 nm, and a plaque thickness of 1/8 inch. The degree of crystallinity for the computations was 40% and was assumed to be constant. Figure 7 clearly indicates that the percent light transmitted increases with decreasing crystallite diameter. The increase is proportionately significant in the lower crystallite size range.

Figure 8, a plot of crystallite diameter versus fumed silica aggregate size in polypropylene, can be used to calculate the size of the crystallites that would result if each one of the fumed silica aggregates would nucleate a site for a crystallite to grow on. The calculations were performed assuming 40% degree of crystallinity, a polypropylene density of 0.91 g/cc, and a fumed silica density of 2.2 g/cc. The plots of Figure 8 are shown at silica loadings of 0.01, 0.1 and 1.0 % by weight.

Based on the above plots, the size of the nucleating and clarifying agent is critical and is preferably less than 0.09 micron to achieve a crystallite size of about 0.3 micron. Most preferred for the nucleating and clarifying agent is a size of less than 0.05 micron. In addition, the nucleating and clarifying agent must be able to be uniformly dispersed in the particular thermoplastic composition. By uniformly



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dispersed is meant that the agent is isolated and well, i. e. uniformly, distributed throughout the composition. As noted above, suitable treating agents may be used to provide compatibility in the system and aid dispersing. Lastly, the agent must possess as little structure as possible meaning that it has reduced branching or enhanced linearity. Although polypropylene and fumed silica have been used for illustrative purposes, it will be appreciated by those skilled in the art that similar plots may be prepared for varying nucleating agents and polymer systems.

Any material having, in combination, the above criteria, namely, small size, low structure and is capable of being uniformly dispersed, will be particularly adapted for use as an effective nucleating and clarifying agent. Such materials include, but is not limited to certain silica sols, precipitated silicas, titanium dioxide, zirconium dioxide and alumina. For example, organically modified silica sols prepared by the precipitation sol gel process will be useful as an effective nucleating and clarifying agents. In particular, sols of monodispersed spheres with an aggregate size diameter of 0.05 microns or less are desirable when used with the appropriate organic modifier and dispersing aid to ensure compatibility with the thermoplastic system. Such sols are commercially available under the name **HIGHLINK® OG** sols (Highlink is a registered trademark of Hoechst AG, Frankfurt, Germany).

Non-limiting illustrations of the destructured fumed silica of the present invention follows.

#### EXAMPLE 1

The destructured fumed silica of the present invention was prepared by charging 125 grams of **CAB-O-SIL® TS-720** fumed silica (**CAB-O-SIL** is a registered trademark of Cabot Corporation) to a one gallon porcelain mill jar (available from U.

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S Stoneware Corp., East Palestine, Ohio) containing approximately 480 - 3/4 inch (19 mm) ceramic balls (available from Fisher-Scientific Corporation, St. Louis, MO). Two grams of acetone were added to the mill jar as an anti-static agent. The mill jars were operated for varying lengths of time depending on the desired degree of destructuring. Samples of the destructured silica were then suspended in amyl acetate for dispersion and de-agglomeration and subjected to sonic energy for approximately 10 minutes. The samples were then placed on a copper grid for examination in Transmission Electron Microscope, viewed at 100,000X magnification. A Kontron Image Analysis Technique was used to determine average aggregate size, average primary particle size and structure. Bulk density was determined by standard techniques for weight and volume measurements. The results are summarized in Table I.

TABLE I

|    | Milling Time<br>(hours) | Bulk Density<br>(lbs/ft <sup>3</sup> ) | Average Aggregate Size<br>(nm) | Structure<br>Parameter* |
|----|-------------------------|--|--------------------------------|-------------------------|
| 15 | 0                       | 3.4                                    | 144.7                          | .4579                   |
|    | 1                       | 17.5                                   | 65.1                           | .6264                   |

\* As stated previously, molten spheres of fumed silica, typically referred to as primary particles, fuse with one another to form branched, three dimensional chain-like aggregates. The configuration of these aggregates differ from one to another. The structure of these aggregates is one measure of the degree of branching of the configuration of the primary particles in the fumed silica aggregates. The structure, as defined herein, is the ratio of the convex perimeter to the perimeter of the two dimensional image of an aggregate as viewed in a TEM. The convex perimeter is the smaller of the two perimeters and is the length of an imaginary line transcribed tightly

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around the two dimensional image of the aggregate. This line does not go into any of the valleys and/or crevices of the aggregate. The perimeter, on the other hand, is the actual outside length of the imaginary line as transcribed around the aggregate's image. The ratio of the two has been termed the structure parameter. By definition, the structure parameter will vary inversely with the branching or the actual structure/morphology of the aggregate. The closer the structure parameter is to zero, the higher the actual structure. The closer the structure is to one, the lower the recorded structure/morphology of the aggregate, i.e. the more destructured the aggregate will be.

As shown in Table I, the average aggregate size is significantly reduced during the ball milling process while the amount of destructuring is increased, as indicated by the structure parameter and bulk density measurements.

## EXAMPLE 2

Same procedure as Example 1 except 100 grams of destructured Cab-O-Sil® M-5 fumed silica was charged to the one gallon porcelain mill jar. The BET surface area for determining nitrogen adsorbed was also calculated using a Gemini 2375 Instrument (available from Micromeritics, Inc., Norcross, GA).

TABLE II

| Milling Time<br>(hours) | Surface Area<br>(m <sup>2</sup> /g) | Bulk Density<br>(lbs/ft <sup>3</sup> ) | Average Aggregate Size<br>(nm) | Structure<br>Parameter* |
|-------------------------|-------------------------------------|--|--------------------------------|-------------------------|
| 0                       | 195.7                               | 3.4                                    | 142.8                          | .4487                   |
| 1                       | 189.0                               | 16.2                                   | 101.8                          | .5518                   |

\* As defined in Table I.

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As shown in Table II, the average aggregate size of the destructured fumed silica is significantly reduced during the ball milling process while the amount of destructuring is increased, as indicated by the structure parameter and bulk density measurements.

5           Examples 3 to 6 are directed to making a masterbatch or concentrate of the destructured fumed silica of the present invention for further blending or compounding into various thermoplastic systems. Example 7 is directed to a dispersion of the destructured fumed silica for further blending or compounding into various thermoplastic systems.

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### EXAMPLE 3

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The destructured fumed silica of Example 2 was used to make a masterbatch in polypropylene by using a twin screw extruder having 85 cc capacity preparation mixer (Brabender Plasticorder® extruder available from C. W. Brabender, Hakensack, NJ). The mixer was preheated to 200°C and the drive was set to run at 5 RPMs. Approximately 49.5 grams of base Quantum Petrothene® 8310 GO polypropylene was added to the mixer and brought to a melt in approximately 10 minutes. Approximately 2.8 grams of calcium stearate was then as an internal lubricant. A total of about 2.8 grams of the destructured fumed silica was added in approximately 1 gram increments. Total incorporation time and maximum developed torque were recorded. The drive was controlled from 5 to 15 RPMs and the compound was mixed for about 5 minutes before increasing the speed to 25 RPMs and mixing for an additional 5 minutes. The extruder blend was collected and ground for molding plaques for further characterization. The final concentration of destructured fumed silica and calcium stearate was approximately 5% by weight.

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#### EXAMPLE 4

Similar to Example 3 except 5.5 grams of destructured fumed silica and calcium stearate was used, thus yielding a final concentration of approximately of 10% by weight.

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#### EXAMPLE 5

Similar to Example 3 except 11.0 grams of destructured fumed silica and calcium stearate was used, thus yielding a final concentration of approximately of 20% by weight.

#### EXAMPLE 6

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Similar to Example 3 except FINA polypropylene (FINA Oil & Chemical Co., LaPorte, TX) was used as the base polymer and no additional internal lubricants were used. The final concentration of fumed silica was approximately 1% by weight.

#### EXAMPLE 7

15

Approximately 140 grams of the destructured fumed silica of Example 2 was mixed in 560 grams of Drakeol mineral oil at low speed with a bench scale mixer which has been fitted with Cowles blades (Chemineer Inc., Dayton, OH). The fumed silica and oil mixture was then charged to a 0.4 liter capacity Eiger Mill (Eiger Machinery, Inc., Mundelein, IL). The first portion of the material was discarded and the remaining material was passed through the mill three more times. The material was then deaerated under full vacuum (30 in of mercury) using a Drais mixer (Drais Werk GmbH, Mannheim Waldof).

20

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## EXAMPLE 8

Approximately 50.3 grams of CAB-O-SIL® PTG fumed silica, a fumed silica having a BET surface area of about 200 m<sup>2</sup>/g and a density of about 2.5 lbs/ft<sup>3</sup>, was mixed with approximately 1400 ml of heptane in a 5000 ml three neck flask equipped with a glass stir rod, an addition funnel and a Dean Stark flask. The fumed silica and heptane mixture was stirred for 5 minutes before adding 4.55 g of octyltriethoxysilane which was dissolved in 20.0 ml of heptane. Upon completion of the addition of octyltriethoxysilane, the addition funnel was removed and the entire mixture was allowed to reflux for 4 hours. The mixture was then allowed to cool to room temperature before filtering and drying under a vacuum. The octyltriethoxysilane treated fumed silica was then ball milled according to the procedure described in Example 1 for incorporation into the masterbatch, as described in Example 3.

## EXAMPLE 9

Similar to Example 8, except phenyltriethoxysilane was used as a treating agent.

## EXAMPLE 10

The masterbatch of Example 6 was further blended with the same base polymer to yield a final concentration of 0.25% by weight fumed silica. Test plaques, having a size of 147 x 63.5 x 2.7 mm, were injection molded using a Battenfield BA 300 CD plus injection molder. Differential Scanning Calorimetry (DSC) Studies were conducted on a TA Instrument DSC 10 System to determine the peak crystallization temperature (T<sub>c</sub>) on cooling. A sample of the polypropylene/fumed silica blend was cooled from about 200°C at a cooling rate of



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10°C per minute. Transmissibility studies were also performed using a wavelength of white light of 550 nm. The results are shown in Table III.

TABLE III

| 5 | Concentration<br>(% by weight) | T <sub>c</sub><br>(°C) | Transmissibility<br>(%) |
|---|--------------------------------|------------------------|-------------------------|
|   | 0.00                           | 112.6                  | 31.7                    |
|   | 0.25                           | 116.9                  | 40.9                    |

10 Table III shows that the percent light transmission increased from 31.7% to 40.9% when the fumed silica of the present invention was incorporated into polypropylene, thus yielding an improvement in clarity. In addition, the transmission was increased when compared to commonly used nucleating agents. Furthermore, an increase from 112.6°C to 116.9°C in peak crystallization temperature is realized when the fumed silica of the present invention was incorporated into polypropylene, thus allowing for increased cycle time.

15 As described herein, the fumed silica of the present invention has been found particularly useful as an effective nucleating and clarifying agent in thermoplastic compositions. Such compositions have improved clarity and can be achieved with low percentages of fumed silica. In addition, processing is improved, e.g. more consistent product performance, reduced mold times and the like, while achieving  
20 desirable aesthetic characteristics.

It is understood that the present invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the scope and spirit of the invention.

25 What is claimed is:

- 20 -

### CLAIMS

1. A fumed silica having an average aggregate size of less than .09  $\mu\text{m}$ .
2. The fumed silica according to claim 1 wherein said fumed silica has a bulk density greater than 2.5 lbs/ft<sup>3</sup>.
- 5 3. The fumed silica according to claim 1 wherein said fumed silica has a bulk density greater than 10 lbs/ft<sup>3</sup>.
4. The fumed silica according to claim 1 wherein said fumed silica has a BET surface area between about 30 m<sup>2</sup>/g and about 500 m<sup>2</sup>/g.
- 10 5. The fumed silica according to claim 1 wherein said fumed silica has an average aggregate size ranging from about 0.01  $\mu\text{m}$  to about 0.07  $\mu\text{m}$ .
6. The fumed silica according to claim 1 wherein said fumed silica is destructured.
7. The fumed silica according to claim 6 wherein said aggregates are physically fractured.
- 15 8. The fumed silica according to claim 1 wherein said fumed silica is treated with a treating agent selected from the group consisting of: straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or amides, nitriles, ethers, silanes, siloxanes and polymers derived therefrom.

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9. A fumed silica having an average aggregate size of less than .09  $\mu\text{m}$  particularly adapted for use as an effective nucleating and clarifying agent in thermoplastic compositions.

5 10. The fumed silica according to claim 9 wherein said fumed silica has a bulk density greater than 2.5 lbs/ft<sup>3</sup>.

11. The fumed silica according to claim 10 wherein said fumed silica has a bulk density greater than 10 lbs/ft<sup>3</sup>.

12. The fumed silica according to claim 9 wherein said fumed silica has a BET surface area between about 30 m<sup>2</sup>/g and about 500 m<sup>2</sup>/g.

10 13. The fumed silica according to claim 9 wherein said fumed silica has an average aggregate size ranging from about 0.01  $\mu\text{m}$  to about 0.07  $\mu\text{m}$ .

14. The fumed silica according to claim 9 wherein said fumed silica is destructured.

15 15. The fumed silica according to claim 14 wherein said aggregates are physically fractured.

16. The fumed silica according to claim 9 wherein said fumed silica is treated with a treating agent selected from the group consisting of: straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or amides, nitriles, ethers, silanes, siloxanes and polymers derived therefrom.

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17. A masterbatch composition for use in polymer compounding comprising:
- (a) a polymer selected from the group consisting of: polyolefins, polyesters, polyimides, polyamides and combinations thereof; and
  - (b) about 5 % to about 40 % by weight of a fumed silica having an average aggregate size of less than .07  $\mu\text{m}$ .
18. The masterbatch composition according to claim 17 wherein said fumed silica has a bulk density greater than 2.5 lbs/ft<sup>3</sup>.
19. The masterbatch composition according to claim 17 wherein said fumed silica has a bulk density greater than 10 lbs/ft<sup>3</sup>.
20. The masterbatch composition according to claim 17 wherein said fumed silica has a BET surface area between about 30 m<sup>2</sup>/g and about 500 m<sup>2</sup>/g.
21. The masterbatch composition according to claim 17 wherein said fumed silica has an average aggregate size ranging from about 0.01  $\mu\text{m}$  to about 0.07  $\mu\text{m}$ .
22. The masterbatch composition according to claim 17 wherein said fumed silica is destructured.
23. The masterbatch composition according to claim 22 wherein said aggregates are physically fractured.
24. The masterbatch composition according to claim 17 wherein said fumed silica is treated with a treating agent selected from the group consisting of: straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or amides, nitriles, ethers, silanes, siloxanes and polymers derived therefrom.

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25. The masterbatch composition according to claim 17 wherein said composition has about 10% to about 20% by weight fumed silica.

26. The masterbatch composition according to claim 17 wherein said fumed silica is incorporated into said masterbatch as part of a dispersion.

5 27. The masterbatch composition according to claim 17 wherein said dispersion comprises a dispersing aid selected from the group consisting of: lubricants, waxes, mineral oil, silicone oil, calcium stearate, stearic acid, and glycol monostearate.

28. A dispersion for use in polymer compounding comprising:

10 (a) a dispersing aid selected from the group consisting of: lubricants, waxes, mineral oil, silicone oil, calcium stearate, stearic acid, and glycol monostearate; and

(b) about 5% to about 40% by weight of a fumed silica having an average aggregate size of less than  $.09 \mu\text{m}$ .

15 29. The dispersion according to claim 28 wherein said fumed silica has a bulk density greater than  $2.5 \text{ lbs/ft}^3$ .

30. The dispersion according to claim 28 wherein said fumed silica has a bulk density greater than  $10 \text{ lbs/ft}^3$ .

31. The dispersion according to claim 28 wherein said fumed silica has a BET surface area between about  $30 \text{ m}^2/\text{g}$  and about  $500 \text{ m}^2/\text{g}$ .

20 32. The dispersion according to claim 28 wherein said fumed silica has an average aggregate size ranging from about  $0.01 \mu\text{m}$  to about  $0.07 \mu\text{m}$ .

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33. The dispersion according to claim 28 wherein said fumed silica is destructured.

34. The dispersion according to claim 33 wherein said aggregates are physically fractured.

5 35. The dispersion according to claim 28 wherein said fumed silica is treated with a treating agent selected from the group consisting of: straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or amides, nitriles, ethers, silanes, siloxanes and polymers derived therefrom.

10 36. The dispersion according to claim 28 wherein said dispersion is about 10% to about 20% by weight fumed silica.

37. A composition having improved transparency and processibility which comprises:

(a) a polymer selected from the group consisting of: polyolefins, polyesters, polyimides, polyamides and combinations thereof; and

15 (b) a fumed silica having an average aggregate size of less than .09  $\mu\text{m}$ .

38. The composition according to claim 37 wherein said fumed silica has a bulk density greater than 2.5 lbs/ft<sup>3</sup>.

39. The composition according to claim 37 wherein said fumed silica has a bulk density greater than 10 lbs/ft<sup>3</sup>.

20 40. The composition according to claim 37 wherein said fumed silica has a BET surface area between about 30 m<sup>2</sup>/g and about 500 m<sup>2</sup>/g.



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41. The composition according to claim 37 wherein said fumed silica has an average aggregate size ranging from about 0.01  $\mu\text{m}$  to about 0.07  $\mu\text{m}$ .

42. The composition according to claim 37 wherein said fumed silica is destructured.

5 43. The composition according to claim 42 wherein said aggregates are physically fractured.

44. The composition according to claim 37 wherein said fumed silica is treated with a treating agent selected from the group consisting of: straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or  
10 amides, nitriles, ethers, silanes, siloxanes and polymers derived therefrom.

45. The composition according to claim 37 wherein said fumed silica is incorporated into said composition as part of a masterbatch.

46. The composition according to claim 37 wherein said fumed silica is incorporated into said composition as part of a dispersion.

15 47. The composition according to claim 46 wherein said dispersion comprises a dispersing aid selected from the group consisting of: lubricants, waxes, mineral oil, silicone oil, calcium stearate, stearic acid, and glycol monostearate.

48. A composition comprising a polymer and from about 0.1% to about 1.0% by weight fumed silica having an average aggregate size less than 0.09 microns.

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49. The composition according to claim 48 wherein said polymer is selected from the group consisting of: polyolefins, polyesters, polyimides, polyamides and combinations thereof.
50. The composition according to claim 48 wherein said fumed silica has a bulk  
5 density greater than 2.5 lbs/ft<sup>3</sup>.
51. The composition according to claim 48 wherein said fumed silica has a bulk density greater than 10 lbs/ft<sup>3</sup>.
52. The composition according to claim 48 wherein said fumed silica has a BET surface area between about 30 m<sup>2</sup>/g and about 500 m<sup>2</sup>/g.
- 10 53. The composition according to claim 48 wherein said fumed silica has an average aggregate size ranging from about 0.01  $\mu$ m to about 0.07  $\mu$ m.
54. The composition according to claim 48 wherein said fumed silica is destructured.
- 15 55. The composition according to claim 54 wherein said aggregates are physically fractured.
56. The composition according to claim 48 wherein said fumed silica is treated with a treating agent selected from the group consisting of: straight chain and branched hydrocarbons, amines, alcohols, glycols, carboxylic acids, esters, and/or amides, nitriles, ethers, silanes, siloxanes and polymers derived therefrom.

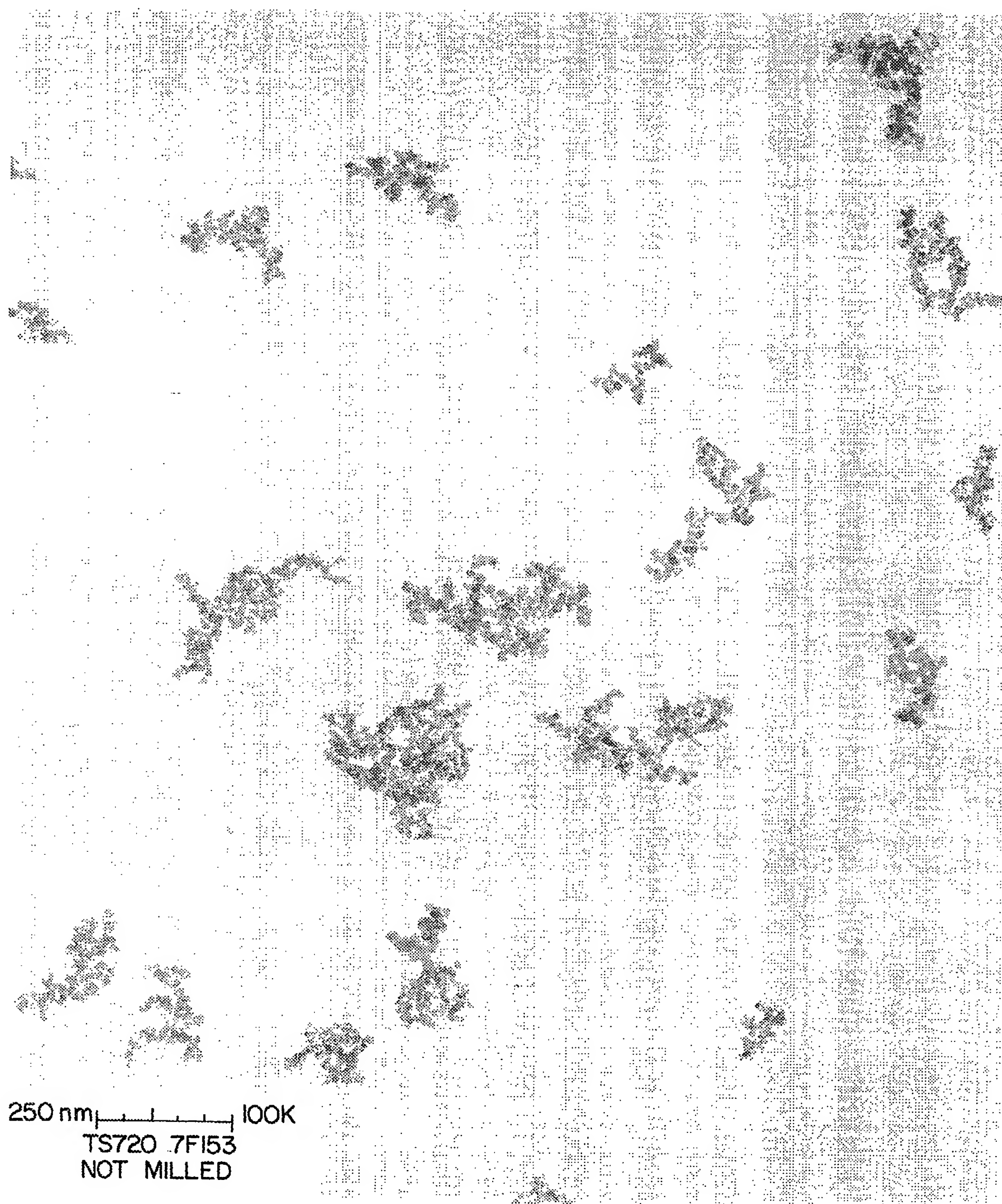


FIG. 1



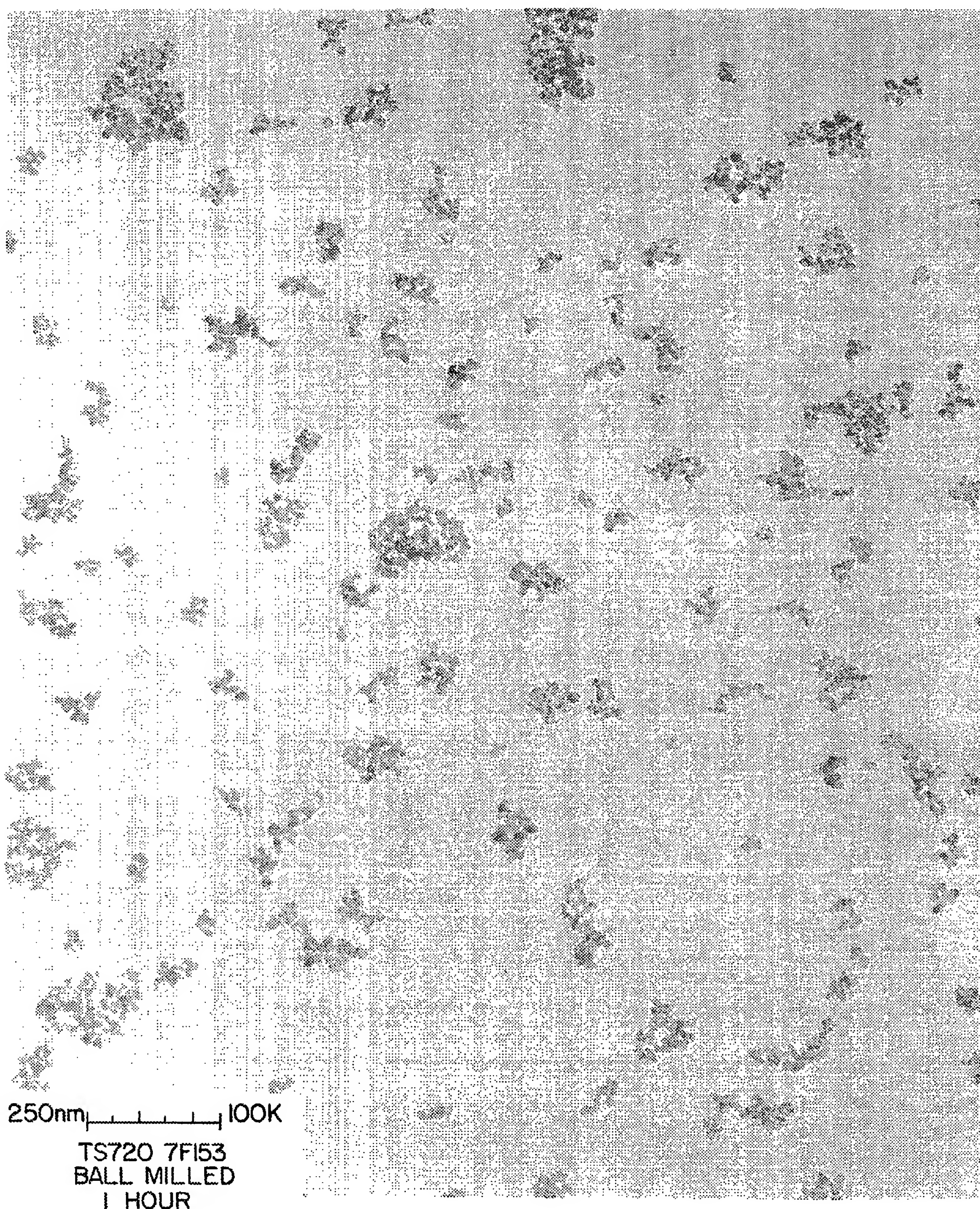


FIG. 2



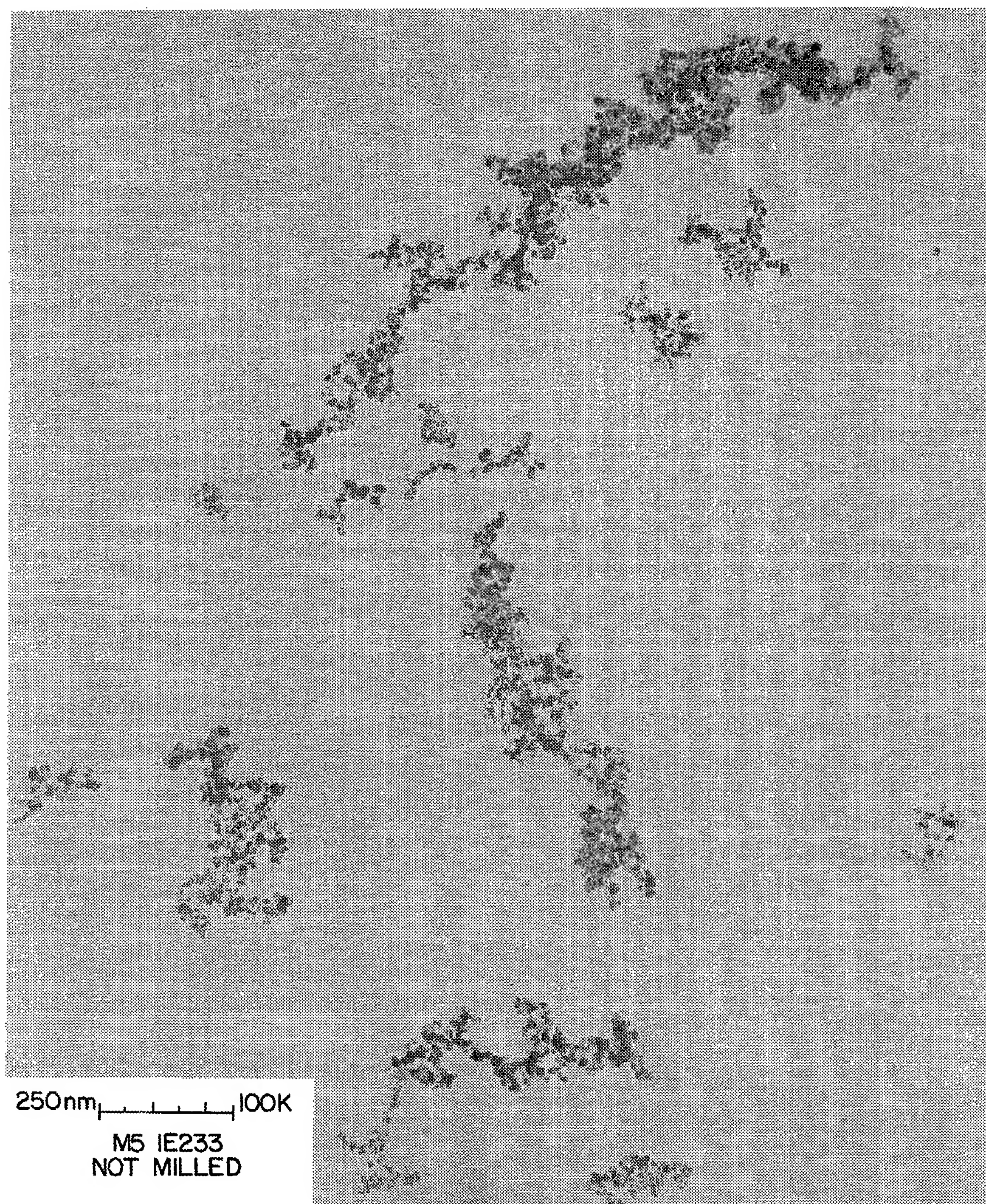


FIG. 3



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FIG. 4



FIG. 5

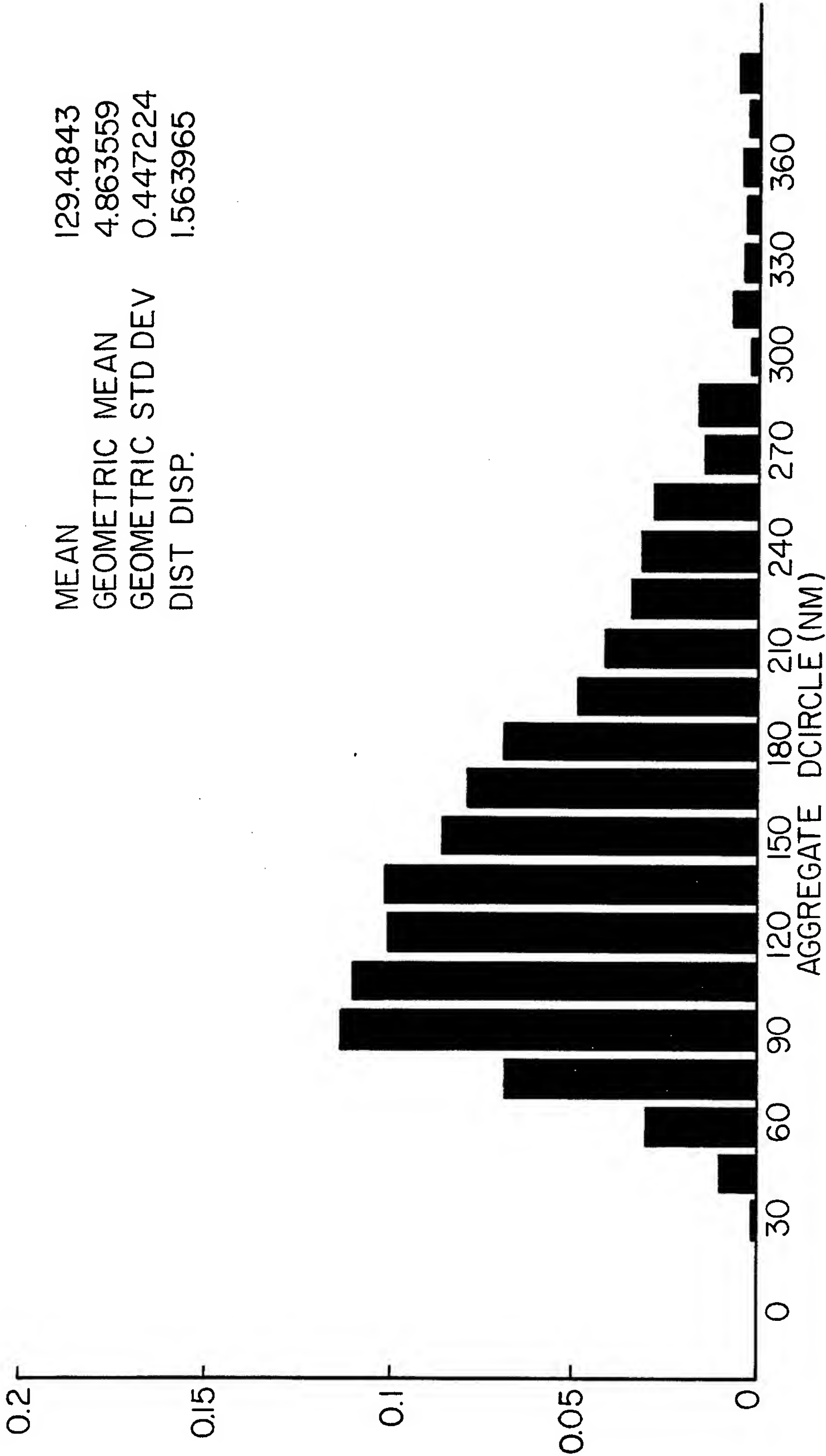
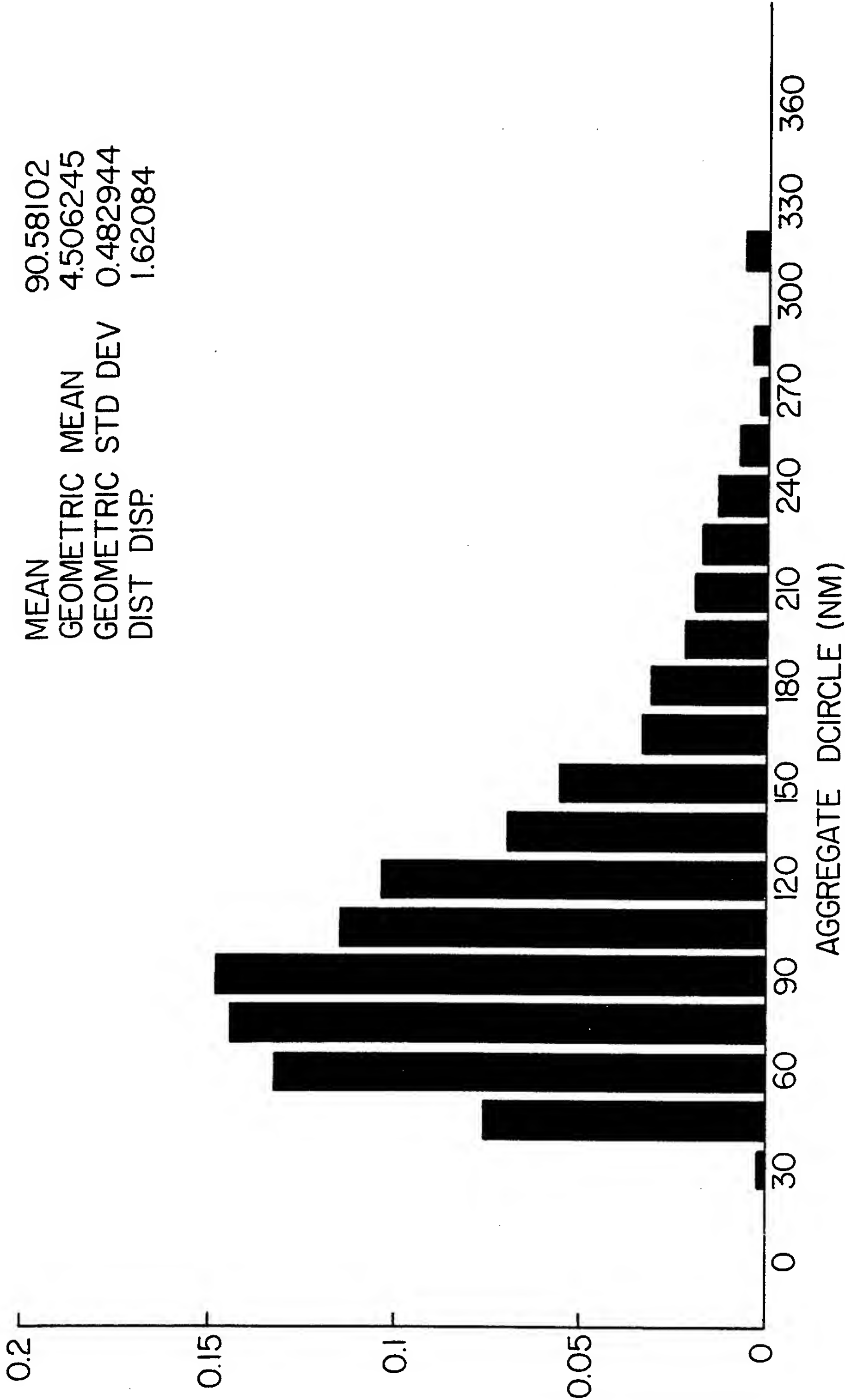
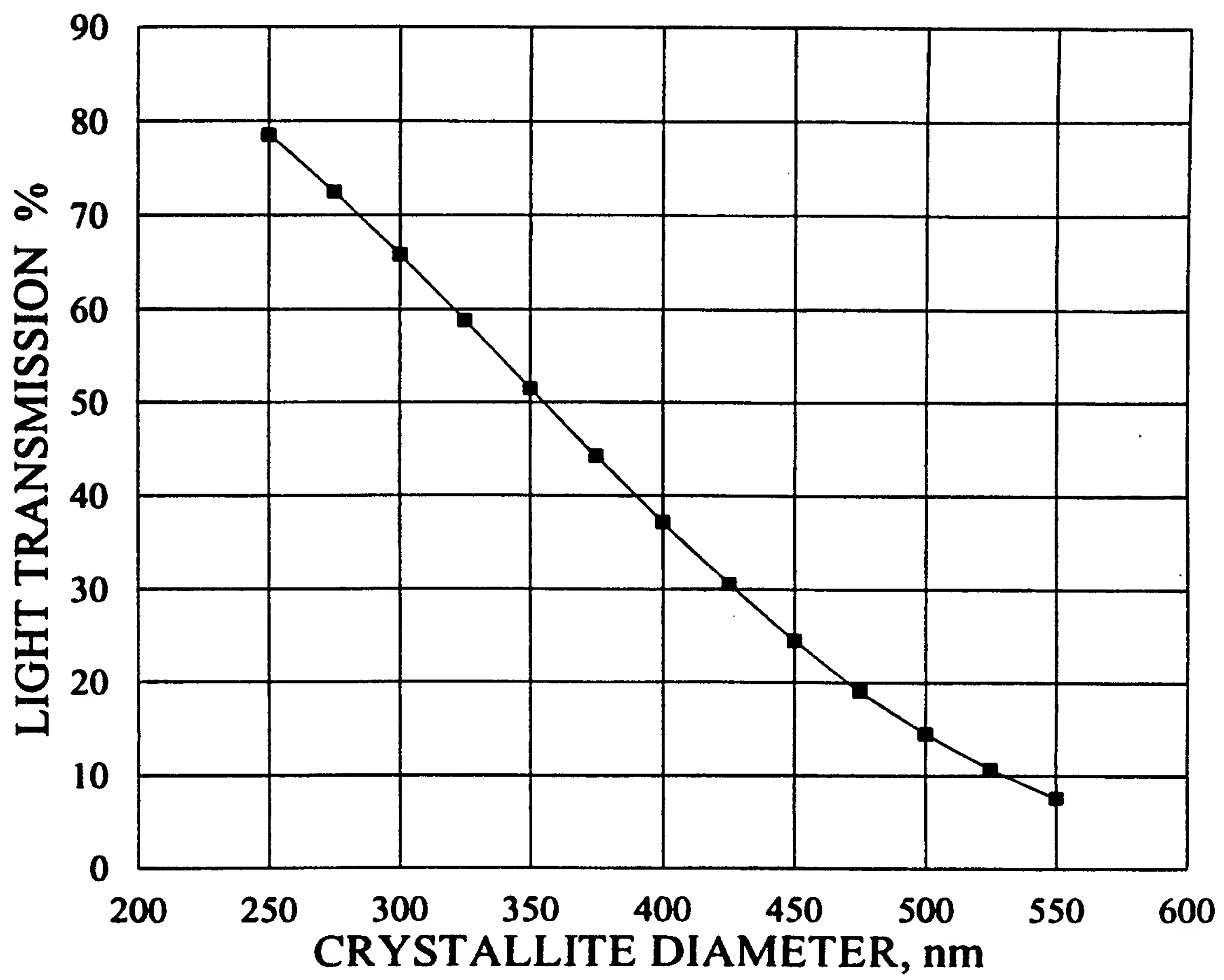


FIG. 6



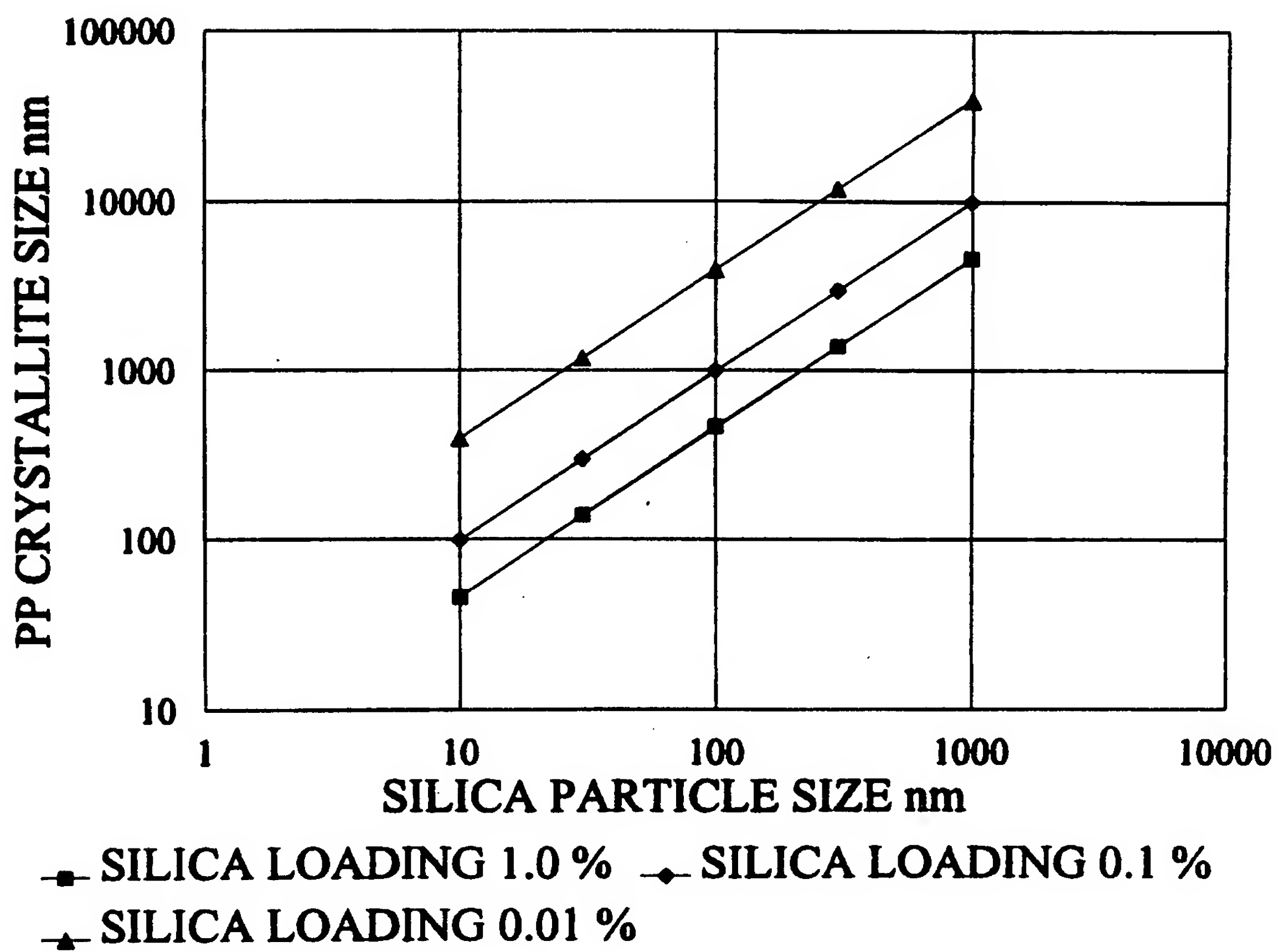
7/8

FIG. 7



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FIG. 8



# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 94/11415

## A. CLASSIFICATION OF SUBJECT MATTER

C 08 K 3/36, C 08 K 9/04, C 01 B 33/18, C 08 L 23/02,  
C 08 L 23/12

According to International Patent Classification (IPC) or to both national classification and IPC 6

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 K, C 08 L, C 01 B, C 09 C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.  |
|------------|--|--|
| X          | RÖMPP CHEMIE LEXIKON,<br>"Aerosil", vol. 1,<br>9th edition, issued 1989,<br>Georg Thieme Verlag-<br>-Stuttgart-New York,<br>page 65.                 | 1, 2, 4,<br>9, 10,<br>12                                       |
| X          | US, A, 4 722 952<br>(HATT) 02 February 1988<br>(02.02.1988),<br>column 1, lines 10-28;<br>column 2, line 18 - column 3,<br>line 9; examples; claims. | 1, 2, 4,<br>6-10,<br>12,<br>14-16,<br>37, 38,<br>40, 42,<br>43 |
| X          | WO, A, 86/02 088<br>(BATELLE DEVELOPMENT<br>CORPORATION) 10 April 1986<br>(10.04.86),  | 1-5,<br>17-21,<br>24,<br>37-41,                                |

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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Date of the actual completion of the international search  
21 December 1994

Date of mailing of the international search report

17. 01. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

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# INTERNATIONAL SEARCH REPORT

Inter      nal Application No  
PCT/US 94/11415

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.                                  |
|------------|---|--|
|            | <p>page 1, line 23 - page 4,<br/>line 24; page 7, line 9 -<br/>page 9; page 14, lines 1-29;<br/>examples, claims.<br/>--</p>  | 47-53  |
| X          | <p>US, A, 4 699 734<br/>(KENDALL et al.) 13 October<br/>1987 (13.10.87),<br/>column 1, line 53 - column 2,<br/>line 62; column 3, line 54 -<br/>- column 5, line 33; claims.<br/>--</p> | <p>1-5,<br/>17-21,<br/>24,<br/>37-41<br/>47-53</p>     |
| X          | <p>US, A, 4 405 729<br/>(SCHWEITZER) 20 September<br/>1983 (20.09.83),<br/>column 1, lines 58-66;<br/>column 3, lines 1-58;<br/>example; claims.<br/>----</p>                           | <p>1, 4-9,<br/>12-16,<br/>28,<br/>31-44,<br/>46-56</p> |

# ANHANG

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

# ANNEX

to the International Search  
Report to the International Patent  
Application No.

# ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 94/11415 SAE 98946

In diesem Anhang sind die Mitglieder  
der Patentfamilien der in obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
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|--|--|--|--|
| US A 4722952   | 02-02-88   | keine - none - rien  |  |
| WD A1 8602088  | 10-04-86   | AT E 49012<br>CA A1 1276363<br>DE C0 3574982<br>EP A1 204714<br>EP B1 204714<br>JP T2 62500457<br>US A 4603158 | 15-01-90<br>13-11-90<br>01-02-90<br>17-12-86<br>27-12-89<br>26-02-87<br>29-07-86 |
| US A 4699734   | 13-10-87   | CA A1 1266338  | 27-02-90   |
| US A 4405729   | 20-09-83   | keine - none - rien  |  |